



## Effect of supports and solvents on ethylene polymerization with titanium complex consisting of phenoxy-imine ligands/dMMAO catalytic system

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### ABSTRACT

Ethylene polymerization by titanium complex having two phenoxy-imine with different supports and solvents has been investigated. It was found that the catalytic activity depended on supports used, and especially on the types of solvent medium. For the supported system, catalytic activities decreased in the following order:  $\text{TiO}_2 > \text{TiO}_2\text{-SiO}_2 > \text{SiO}_2$ . This can be attributed to the strong interaction of the  $\text{TiO}_2$  with dried MMAO (dMMAO) and the larger amount of dMMAO present on the  $\text{TiO}_2$  than other supports. Furthermore, the catalytic activity was significantly affected by the solvent medium. According to the homogeneous system, the catalytic activities increased in the order of: toluene > heptane > chlorobenzene  $\gg$  dichloromethane up on difference solvent mediums. On the other hand, for the supported system, the catalytic activity was the highest when heptane was employed. In order to give a better explanation, the different types of ion-pairs formed was proposed. The properties of polymers were further discussed in more details.

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### 1. Introduction

Nowadays, polymer and plastics are playing the important role on the material industry. This is because they exhibit many useful properties, such as low density, high strength, and resistance to chemical attack, as well as being cost-effective. Otherwise the demands for the plastics increase in huge quantities every year. Among synthetic polymers, polyethylene is the major polymer and the largest of production in plastic industry [1–3].

It is well known that research and development of high-performance olefin polymerization catalysts have contributed significantly to the advancement of organometallic chemistry and polymer chemistry and have made a dramatic impact on the polyolefin industry. A recent example is the discovery of group 4 metallocene catalysts, which displays very high ethylene polymerization activity [4–6]. More recently, other classes of transition metal complex have been investigated as precursor for a new generation of olefin polymerization catalyst [7–12]. Specifically, olefin polymerization catalysts have been developed from nickel or palladium complexes with diimine [7,8], iron or cobalt complexes with diimine–pyridine ligands [9,10], titanium with diamide ligands [11,12]. Furthermore, Fujita and his co-workers [13] have

successfully established highly active titanium and zirconium catalysts using various substituted phenoxy-imine ligands for olefin polymerization, which were named as FI catalysts. Depending on the ligand design, the catalyst showed different behaviors in ethylene and propylene polymerization, and the ligands strongly influenced catalytic parameters such as activity, polymerization mechanism, and polymer properties such as molecular weight [14]. Now phenoxy-imine ligands greatly interest more and more researchers [15,16]. It was found that homogeneous catalytic system has two disadvantages; the lack of morphologies control of polymer produced and reactor fouling. Therefore, binding these catalysts onto inorganic supports can provide a promising way to overcome these drawbacks. It has been reported that many inorganic supports such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{MgCl}_2$  have been extensively studied [17,18].

In this present study, the effect of different supports/dMMAO with titanium complex having phenoxy-imine catalyst on ethylene polymerization was investigated. The supports such as  $\text{TiO}_2$ ,  $\text{SiO}_2$ , and  $\text{TiO}_2\text{-SiO}_2$  mixed oxide were employed. The effect of solvent mediums used in slurry polymerization of ethylene was also investigated. The solvent mediums such as heptane, toluene, chlorobenzene (CB), and dichloromethane (DCM) having different dielectric constant value ( $\epsilon$ ) were used. The catalytic activities during ethylene polymerization were monitored and further discussed. The microstructure of polymer obtained was also investigated.

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## 2. Experimental

### 2.1. Materials

All operations were handled under an argon atmosphere using glove box and/or standard Schlenk techniques. Ethylene (polymerization grade) was obtained from the National Petrochemical Co., Ltd., Thailand. 3-*tert*-Butylsalicylaldehyde was purchased from Aldrich Chemical Company, Inc., and used without further purification.  $\text{TiCl}_4$  (99+%) was purchased from Aldrich Chemical Company, Ltd., and used without further purification. Aniline and tetrahydrofuran (Anhydrous grade) were purchased from Aldrich Chemical Company, Inc. Heptane and chlorobenzene were purchased from Fluka Chemie, A.G., Switzerland and purified by distilling over sodium under argon atmosphere before used. Modified methylaluminoxane, MMAO (1.86 M in toluene) was donated by Tosoh Akzo, Japan. Silica gel (Cariact P-10) came from Fuji Silysia Chemical, Ltd., Japan. Titanium(IV) oxide (pure anatase) was obtained from Aldrich Chemical Company. Toluene was donated by the Exxon Chemical, Thailand Co., Ltd. It was dried over dehydrated  $\text{CaCl}_2$  and distilled over sodium/benzophenone. Ultra-high purify (UHP) argon (99.999%) was purchased from Thai Industrial Gas Co., Ltd., and was further purified by passing through molecular sieves 3 Å, BASF catalyst R3-11G, NaOH and phosphorus pentaoxide ( $\text{P}_2\text{O}_5$ ) to remove traces oxygen and moisture.

### 2.2. Preparation of $\text{SiO}_2$ - $\text{TiO}_2$ mixed oxide support

Each  $\text{SiO}_2$ - $\text{TiO}_2$  mixed oxide support [surface area of  $\text{SiO}_2 = 281 \text{ m}^2 \text{ g}^{-1}$  and  $\text{TiO}_2 = 70 \text{ m}^2 \text{ g}^{-1}$ ] was prepared according to the method described by Conway et al. [19]. In particular, 1 g of  $\text{SiO}_2$ - $\text{TiO}_2$  (4:1 by weight) [20] mixed oxide support was physically mixed by dispersing in toluene (ca. 20 mL). The mixture was stirred for 30 min, filtered, and then dried under vacuum.

### 2.3. Removal of trialkylaluminiums from MMAO

Removal of trialkylaluminiums from MMAO was carried out according to the reported procedure [21]. The toluene solution of MMAO was dried under vacuum for 6 h at room temperature to evaporate the solvent,  $\text{AlMe}_3$ , and  $\text{Al}(\text{iBu})_3$ . Then, we continued to dissolve the material with 100 mL of heptanes. Finally, the solution was evaporated under vacuum to remove the remaining  $\text{AlMe}_3$  and  $\text{Al}(\text{iBu})_3$ . This procedure was repeated four times and the white powder of dried MMAO (dMMAO) was obtained.

### 2.4. Preparation of supported dMMAO

Silica-supported dMMAO (dMMAO/ $\text{SiO}_2$ ) was prepared according to the literature [21].  $\text{SiO}_2$  was calcined at 573 K for 6 h. A toluene solution (100 mL) of dMMAO (15 g) was added into the  $\text{SiO}_2$  slurry in toluene (20 g, 250 mL). The mixture was stirred for 30 min at room temperature. After the toluene was evaporated under vacuum, the mixture was washed with hexane (150 mL  $\times$  7) and finally dried under vacuum for 5 h to give  $\text{SiO}_2$ /dMMAO. Similarly, silica-titania mixed oxide-supported dMMAO (dMMAO/ $\text{SiO}_2$ - $\text{TiO}_2$ ) and titania-supported dMMAO (dMMAO/ $\text{TiO}_2$ ) were prepared according to the method as described above.

### 2.5. Titanium complex synthesis

Titanium complex was synthesized by the reaction of  $\text{TiCl}_4$  with two equivalents of salt of the corresponding phenoxy-imine ligands according to the literature [22].

### 2.6. Polymerization procedure

The ethylene polymerization reaction was carried out in a 100-mL semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. First, the reactor was charged with solvent such as heptane, toluene, chlorobenzene, and dichloromethane (to make a total volume of 30 mL) follow by adding the desired amount of supported dMMAO. Then, a solution of catalyst in toluene was added into the reactor having the  $[\text{Al}]_{\text{dMMAO-support}}/[\text{Ti}]_{\text{cat}}$  ratio of 250. The reactor was then immersed in liquid nitrogen. After that, it was evacuated to remove the argon. Then, the reactor was adjusted to the polymerization temperature at 323 K. Polymerization was started by feeding ethylene gas (total pressure 50 psi) until the consumption of ethylene 0.018 mol (6 psi was observed from pressure gauge) was completed. Ethylene pressure and temperature were kept constant during the polymerization, and the consumption rate of ethylene was monitored by a mass flow meter. Polymerization was terminated with acidic methanol. The polymer obtained was precipitated in acidic methanol, filtered, adequately washed with methanol, and finally dried under vacuum at 333 K for 6 h.

### 2.7. Characterization

#### 2.7.1. Characterization of titanium complex catalyst

**Nuclear magnetic resonance spectroscopy:** The  $^1\text{H-NMR}$  spectra were recorded at ambient probe temperature (298 K) using BRUKER AVANCE II 400 operating at 100 MHz with an acquisition time of 1.5 s and a delay time of 4 s. Ligands and titanium complex solution were prepared using tetramethylsilane as solvent and deuterated chloroform for an internal lock.

#### 2.7.2. Characterization of supports and catalyst precursors

**X-ray diffraction:** XRD was performed to determine the bulk crystalline phases of samples. It was conducted using a SIEMENS D-5000 X-ray diffractometer with  $\text{Cu K}\alpha$  ( $\lambda = 1.54439 \text{ \AA}$ ). The spectra were scanned at a range of  $2.4^\circ \text{ min}^{-1}$  in the range  $2\theta = 20$ – $80^\circ$ .

**Scanning electron microscopy and energy dispersive X-ray spectroscopy:** SEM and EDX were used to determine the sample morphologies and elemental distribution throughout the sample granule, respectively. The SEM of JEOL mode JSM-5800LV was applied. EDX was performed using Link Isis series 300 program.

**Thermogravimetric analysis:** TGA was performed using a TA instruments SDT Q 600 analyzer. The samples of 10–20 mg and temperature ramping from 298 to 873 K at  $5 \text{ K min}^{-1}$  were used in the operation. The carrier gas was  $\text{N}_2$  UHP.

**Raman spectroscopy:** The Raman spectra of the samples were collected by projecting a continuous wave YAG lasers of neodymium (Nd) red (810 nm) through the samples at room temperature. A scanning range of  $100$ – $1000 \text{ cm}^{-1}$  with a resolution of  $2 \text{ cm}^{-1}$  was applied.

**FTIR spectroscopy:** FTIR was conducted on a NICOLET series 6700 instruments. The supports (1 mg) were mixed with 100 mg KBr. About 400 scans were accumulated for each spectrum in transmission with a resolution of  $4 \text{ cm}^{-1}$ . The spectrum of dried KBr was used as a background subtraction.

#### 2.7.3. Characterization of polymer

**Scanning electron microscopy and energy dispersive X-ray spectroscopy:** SEM and EDX were performed to study morphologies of polymer produced. The same equipment as mentioned above was employed.

**Differential scanning calorimetry:** DSC thermal analysis measurements were performed using a PerkinElmer DSC P7 calorimeter. The DSC measurements reported here were recorded during the second heating/cooling cycle with the rate of  $20 \text{ K min}^{-1}$ . This procedure

ensured that the previous thermal history was erased and provided comparable conditions for all samples. Approximately 10 mg of sample was used for each DSC measurement.

### 3. Results and discussion

In this present study, the effects and roles of various supported-dMMAOs and solvents on catalytic activities using titanium complex having two phenoxy-imine catalyst systems are discussed as follows.

#### 3.1. Characteristics of the different supports and supported-dMMAOs

First, the different supports before and after impregnation with dMMAO were characterized using many characterization techniques. It was observed that the XRD patterns of the pure  $\text{TiO}_2$  indicated only the characteristic peaks of anatase  $\text{TiO}_2$  at 25 (major), 37, 48, 55, 56, 62, 71, and 75°. It is apparent that the pure silica shown a broad XRD peak assigning to conventional amorphous silica. The XRD patterns of mixed  $\text{TiO}_2$ - $\text{SiO}_2$  supports exhibited the combination of mixed  $\text{TiO}_2$ - $\text{SiO}_2$  supports. Raman spectra of supports are shown in Fig. 1. It was found that the titania support exhibited the Raman band at 639, 516, and 397  $\text{cm}^{-1}$  for titania in anatase form as seen in the literatures [23–25], whereas silica was Raman-insensitive over the scanning range applied. FTIR spectra of the different supports are shown in Fig. 2. Pure silica exhibited a typical spectrum of amorphous silica. The band at 1100  $\text{cm}^{-1}$  was the asymmetrical vibration of the Si–O–Si bond in the tetrahedral  $\text{SiO}_4$  unit of the  $\text{SiO}_2$  matrixes [26]. A broad peak centered at around 650  $\text{cm}^{-1}$  represented the presence of titanium oxide [27] appeared with the introduction of Ti species. A broad peak at 1100  $\text{cm}^{-1}$  appeared for the mixed  $\text{TiO}_2$ - $\text{SiO}_2$  supports showed the combination of mixed  $\text{TiO}_2$ - $\text{SiO}_2$  supports. This band had been ascribed to the vibration involving a  $\text{SiO}_4$  tetrahedron bonded to a titanium atom through Si–O–Ti bonds [28]. The presence of this band confirmed the presence of Si–O–Ti linkages in the  $\text{TiO}_2$ - $\text{SiO}_2$  mixed supported. In order to determine the morphologies and elemental distribution of the supports after impregnation with dMMAO, SEM and EDX were performed, respectively. The SEM and EDX mapping of the different supports are shown in Fig. 3. The EDX mapping of the supports can provide more information about the distribution on each supports. It can be observed that dMMAO was well distributed all over support granules. In addition, the EDX measure-

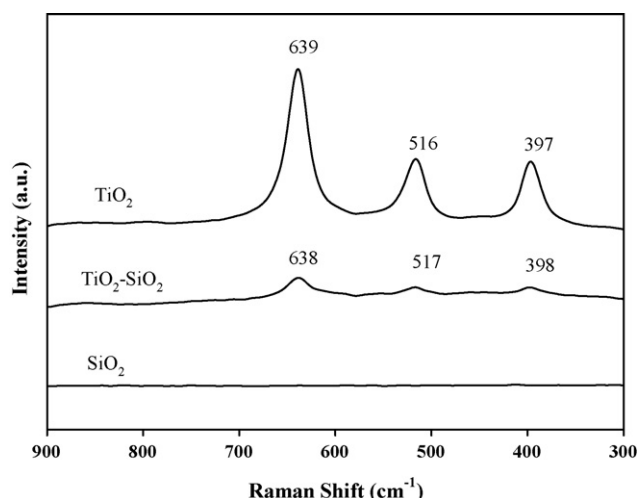


Fig. 1. Raman spectra of different supports before impregnation with dMMAO.

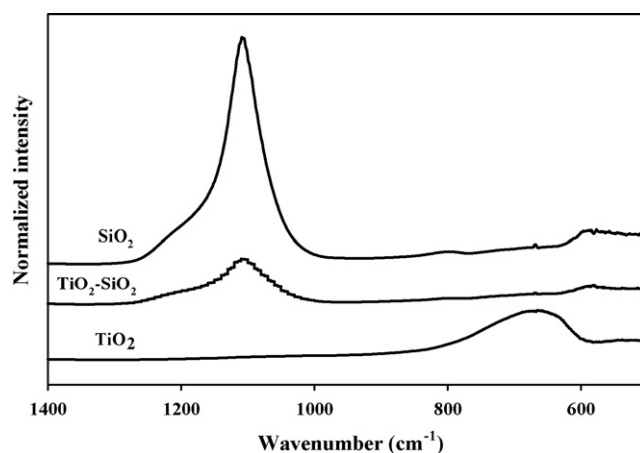


Fig. 2. FTIR spectra of different supports.

ment was also used to determine the concentrations of  $[\text{Al}]_{\text{dMMAO}}$  present on different supports with the EDX spectrum obtained as seen in Fig. 4. It was found that the average amount of  $[\text{Al}]_{\text{dMMAO}}$  on  $\text{TiO}_2$ ,  $\text{TiO}_2$ - $\text{SiO}_2$  and  $\text{SiO}_2$  were 11.07, 10.29, and 9.11 wt.%, respectively. The larger amount of  $[\text{Al}]_{\text{dMMAO}}$  present in the  $\text{TiO}_2$  can be attributed to the strongest interaction among other supports.

#### 3.2. Effect of supports on the catalytic activity

For comparative studies, the catalytic activities towards the polymerization of ethylene upon different supported-dMMAOs were measured. The results are summarized in Table 1. The activities of the supported system were lower than the homogeneous one, as expected. However, considering only the supported system, it was found that activities were in the order of:  $\text{TiO}_2 > \text{TiO}_2$ - $\text{SiO}_2 > \text{SiO}_2$ . It is well known that, the supported system exhibited lower activity than the homogeneous one due to the supporting effect. Among the supported system, the  $\text{TiO}_2$  showed the highest activity (entry 2; 4286 kg PE/(mol cat h)), which was unusual for available literature reports. It was reported that the lowest polymerization activity obtained from zirconocene using the  $\text{TiO}_2$  support was due to strong support interaction [21,25,29]. However, based on our results, the polymerization activity obtained from  $\text{TiO}_2$  was the highest. This indicated that besides the surface concentration of  $[\text{Al}]_{\text{dMMAO}}$ , the interactions between the  $[\text{Al}]_{\text{dMMAO}}$  and different support were quite important. In fact, the strong interaction of species with  $\text{TiO}_2$  or other supports employed in this study was referred to the interaction between the support and the cocatalyst (dMMAO). Based on this study, dMMAO was dispersed by impregnation onto the support prior to polymerization. The degree of interaction between the support and dMMAO can be determined by the TGA measurement. In order to give a better understanding, we propose the interaction of support and dMMAO based on the review paper by Severn et al. [30]. They explained that the connection of the support and cocatalyst occurred via the  $\text{O}_{\text{support-Al cocatalyst}}$  linkage. In particular, the TGA can only provide useful information on the degree of interaction for the dMMAO bound to the support in terms of weight loss and removal temperature. The stronger interaction can result in decreased leaching of dMMAO bound to the different supports to react with the titanium complex catalyst during activation processes, leading to higher catalytic activity for polymerization. It has long been known that the  $\text{TiO}_2$  support is known to have a strong interaction with species present on it. The TGA measurement was performed in order to prove interaction between the  $[\text{Al}]_{\text{dMMAO}}$  and various supports as shown in Fig. 5. We can observe the similar profiles for different sup-

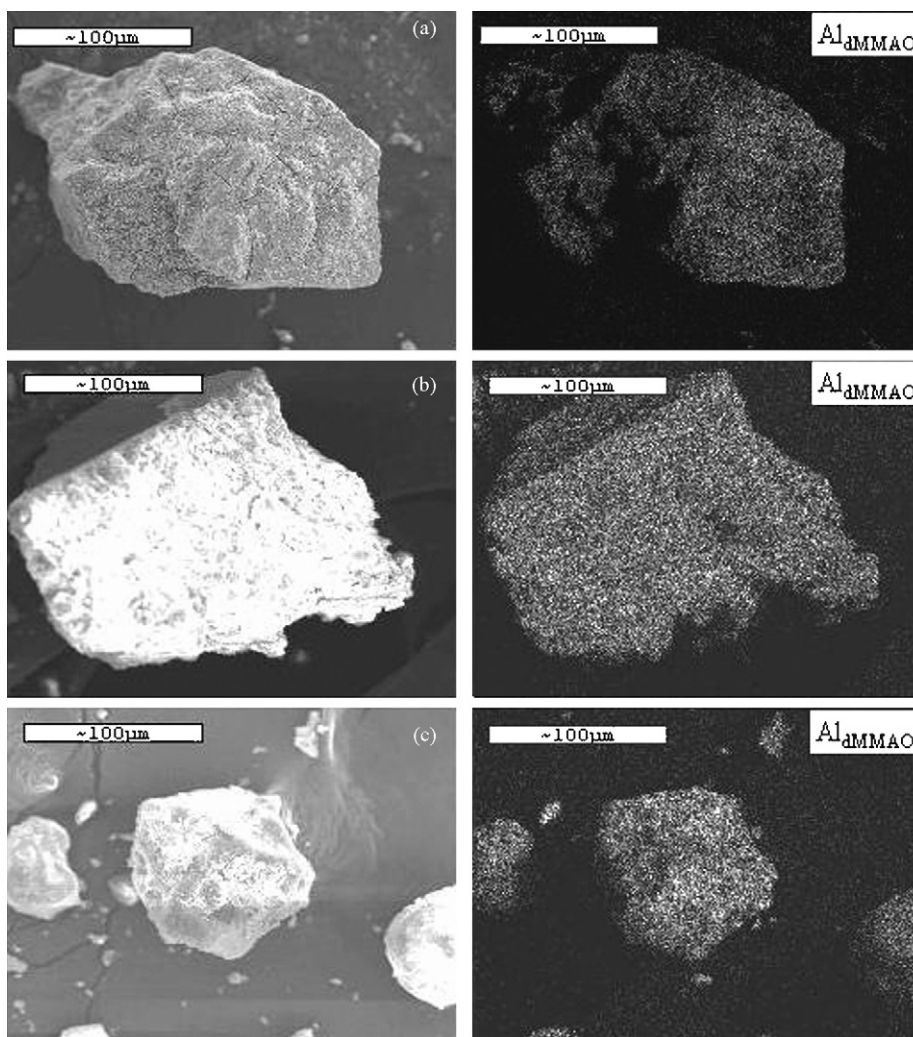


Fig. 3. SEM and EDX mapping of different supports: (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2\text{-SiO}_2$ , and (c)  $\text{SiO}_2$ .

ports. It demonstrated that the weight losses of  $[\text{Al}]_{\text{dMMAO}}$  present on different supports were in order of  $\text{SiO}_2$  (22%) >  $\text{TiO}_2\text{-SiO}_2$  (19.65%) >  $\text{TiO}_2$  (16.36%). This indicated that  $[\text{Al}]_{\text{dMMAO}}$  present on  $\text{TiO}_2$  had the strongest interaction and thus, the highest observed

polymerization activity. Moreover, in the case of  $\text{TiO}_2\text{-SiO}_2$  support, it had stronger interaction than that of  $\text{SiO}_2$ , therefore it exhibited higher polymerization interaction due to higher concentrations of  $[\text{Al}]_{\text{dMMAO}}$  at surface as mentioned above. Besides, the presence of

**Table 1**  
Polymerization<sup>a</sup> results

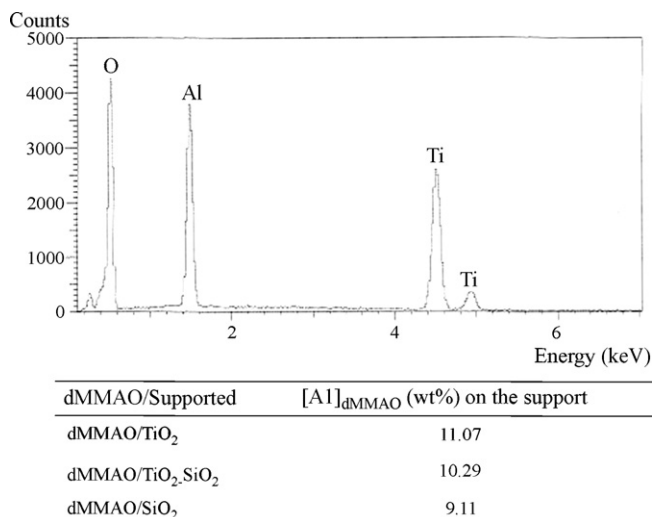
Entry	System	Solvent	Polymerization time (s)	Polymer Yield <sup>b</sup> (g)	Activity (kg PE/(mol cat h))	$T_m$ <sup>c</sup> (K)
1	Homogeneous	Heptane	143	0.449	4521	409
2	$\text{TiO}_2$ support		150	0.446	4286	407
3	$\text{SiO}_2\text{-TiO}_2$ support		169	0.449	3828	406
4	$\text{SiO}_2$ support		174	0.407	3372	406
5	Homogeneous	Toluene	128	0.461	5186	406
6 <sup>d</sup>	Homogeneous		151	0.452	4310	406
7	$\text{TiO}_2$ support		226	0.444	2828	406
8	$\text{SiO}_2\text{-TiO}_2$ support		244	0.470	2782	406
9	$\text{SiO}_2$ support		270	0.441	2350	406
10	Homogeneous	CB	290	0.444	2205	406
11	$\text{TiO}_2$ support		318	0.476	2156	407
12	$\text{SiO}_2\text{-TiO}_2$ support		400	0.480	1727	406
13	$\text{SiO}_2$ support		428	0.489	1646	406

<sup>a</sup> Polymerization condition:  $[\text{Ti}] = 2.5 \mu\text{mol}$ ,  $[\text{Al}]_{\text{dMMAO}}/[\text{Ti}] = 250$ , temperature of polymerization = 323 K.

<sup>b</sup> The polymer yield was fixed by limiting the ethylene fed (0.018 mole equally).

<sup>c</sup> Melting temperature was measured by DSC analysis.

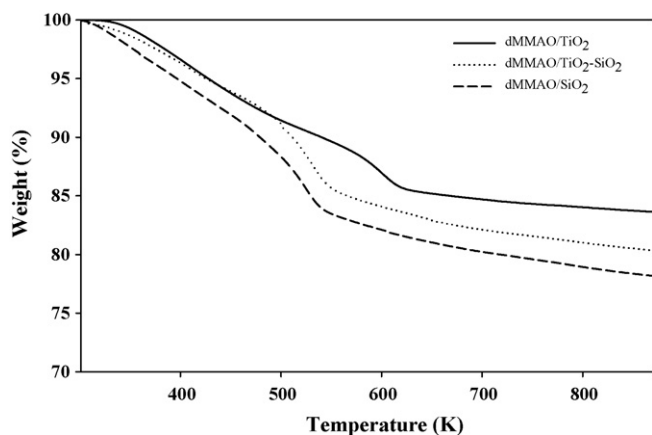
<sup>d</sup> Polymerization condition:  $[\text{Ti}] = 2.5 \mu\text{mol}$ ,  $[\text{Al}]_{\text{MMAO}}/[\text{Ti}] = 250$ , temperature of polymerization = 323 K.



**Fig. 4.** A typical spectrum of the supported-dMMAO from EDX analysis used to measure the average [Al]<sub>dMMAO</sub> concentration on different supports.

TiO<sub>2</sub> in SiO<sub>2</sub> as a spacer group was also responsible for higher activity [20,31]. Furthermore, several researchers reported that TiO<sub>2</sub> had more active species being present during polymerization and removed residual hydroxyl groups from TiO<sub>2</sub> particles resulted in significant increases in catalytic activity of olefin polymerization [32]. Based on the observed polymerization activities, it is worth noting that in order to obtain the high polymerization activity, ones need to consider on high concentration of [Al]<sub>dMMAO</sub> present and the interaction between O<sub>support</sub> and Al<sub>cocatalyst</sub> linkage.

In order to obtain more detailed aspects on catalytic activity in the supported-dMMAO system, we consider the structure of titanium complex catalyst, which has large structure due to two phenoxy-imine ligands as shown on the review paper by Matsui et al. [33]. It is known that an active species of group 4 transition metal complexes for olefin polymerization is an alkyl cationic complex having two available *cis*-locate sites needed for polymerization [34]. It was generated by reaction of catalyst precursors such as dichloro complex with alkylaluminum compound. Therefore, the different supported-dMMAOs as catalyst precursors have shown remarkable effects on the catalytic activity of olefin polymerization. In contrast, we believe that the Al of dMMAO leached from different supports during activation processes caused the lesser amount of active species for polymerization. This hypothesis can be confirmed by the comparative study on catalytic activities between TiO<sub>2</sub> and



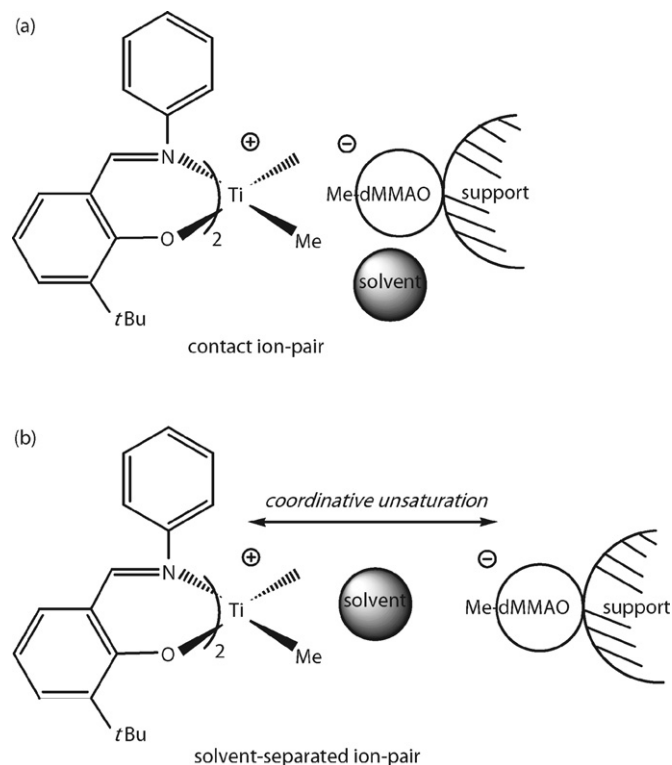
**Fig. 5.** TGA profiles of supported-dMMAO on different supports.

SiO<sub>2</sub> supports, where the use of SiO<sub>2</sub> as support resulted in low catalytic activity due to more leached Al than that of TiO<sub>2</sub>. Furthermore, Matsui et al. [33] reported that the high activity displayed by titanium complex resulted from the fact that a phenoxy-imine ligand possessed moderate electron donating properties and at the same time an active species of the complex had two available *cis* located sites needed for polymerization.

In order to compare the catalytic activity between MMAO and dMMAO, ethylene polymerization using different cocatalysts were conducted. It was observed that combination of titanium complex with dMMAO in toluene showed a higher catalytic activity than that with MMAO as shown in Table 1 (entry 5 and 6). Bryliakov et al. [35] reported that homogeneous polymerizations of  $\alpha$ -olefins with the titanium FI-catalysts (titanium complex) were very sensitive towards trimethylaluminum (TMA), which was always included in the cocatalyst modified methylaluminoxane (MMAO). The amount of free TMA in the MMAO solution can be reduced by removing toluene from the cocatalyst to give a white powder (dMMAO). Additionally, Makio et al. [13] reported that FI-catalysts (titanium complex) were not only sensitive to the addition of TMA, but also to the triisobutylaluminum (TIBA), which was used as scavenger for water and impurities during polymerization. TIBA can attack the imine function of the ligands and reduce it to an amine. Dried modified methylaluminoxane (dMMAO) prepared from mixture of trimethylaluminum (TMA) and triisobutylaluminum (TIBA) can also be used as an activator in case of titanium complex catalyst.

### 3.3. Effect of solvent on the catalytic activity

Ethylene polymerization was conducted in solvent medium that have different dielectric constant values ( $\epsilon$ ). The dielectric constant ( $\epsilon$ ) increases in the following order: heptane ( $\epsilon = 1.92$ ) < toluene ( $\epsilon = 2.38$ ) < chlorobenzene ( $\epsilon = 5.68$ ) < dichloromethane ( $\epsilon = 8.93$ )



**Scheme 1.** A plausible scheme for the interaction between active species and solvent in the supported system: (a) active species in heptane and (b) active species in polar solvents.

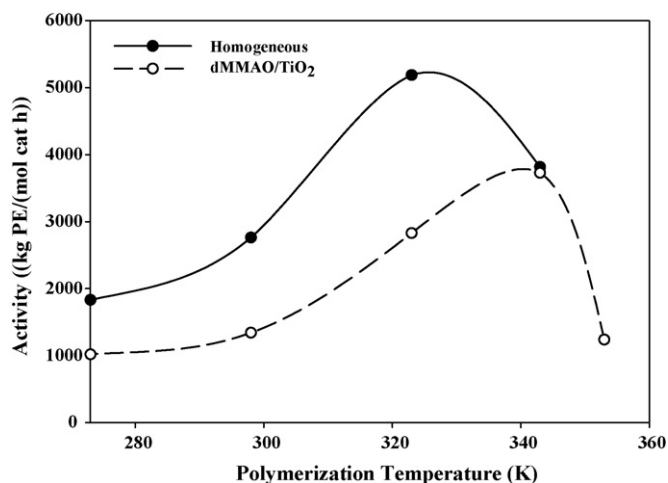


Fig. 6. Temperature dependence of polymerization activity obtained with titanium complex-dMMAO.

[36]. The catalytic activities based on polymer yield are shown in Table 1. For ethylene polymerization in homogeneous system, it was found that when using toluene as the polymerization medium, activity was the highest (entry 5; 5186 kg PE/(mol cat h)) followed by heptane (entry 1; 4521 kg PE/(mol cat h)) and chlorobenzene (entry 10; 2205 kg PE/(mol cat h)), respectively. No activity was observed when dichloromethane was employed. This indicated that the too high dielectric constant of solvent apparently resulted in such a low or no activity. Forlini et al., [37,38] also reported

that the dielectric constant value of solvent could alter the polymerization behavior in other catalytic systems. In all cases, the polymerization did not proceed with the use of dichloromethane as a solvent medium. In the case of the supported system, activities are listed in Table 1. It was found that using heptane (entry 2; 4286 kg PE/(mol cat h)) as the polymerization medium gave the highest activity in all supports followed by toluene and dichlorobenzene, respectively.

It should be noted that the major factor to be considered besides the solvent polarity is the solubility of ethylene up on different solvents. Hence, the solubility of ethylene at polymerization temperature in different solvents was essentially important. Intaragamjon et al., [39] also reported that there was no variation in solubility of ethylene in the various solvents. Thus, the solubility of ethylene was not significant change regarding activity of ethylene polymerization in both homogeneous and supported systems. On the other hand, the catalytic activities observed were attributed to the solvent polarity itself.

In order to obtain more detailed aspects on effect of solvent on catalytic activity, the conceptual model of solvent effect was redrawn based on the work done by Ziegler group [40]. In general, in non-polar solvent, the dominant species is the contact ion-pair, whereas for the aromatic solvent, there are solvent separated ion-pair and solvent complexed cation. Based on the plausible reaction of the contact ion-pair model, the following considerations regarding to the solvent effect can be proposed: (i) considering in homogeneous system, the polarity of solvent greatly affected the polymerization activity. The solvent effect is based on the types of ion-pair formed. The higher activity observed in toluene was not only the reflex of ion-pair separation. In general, chlorinated

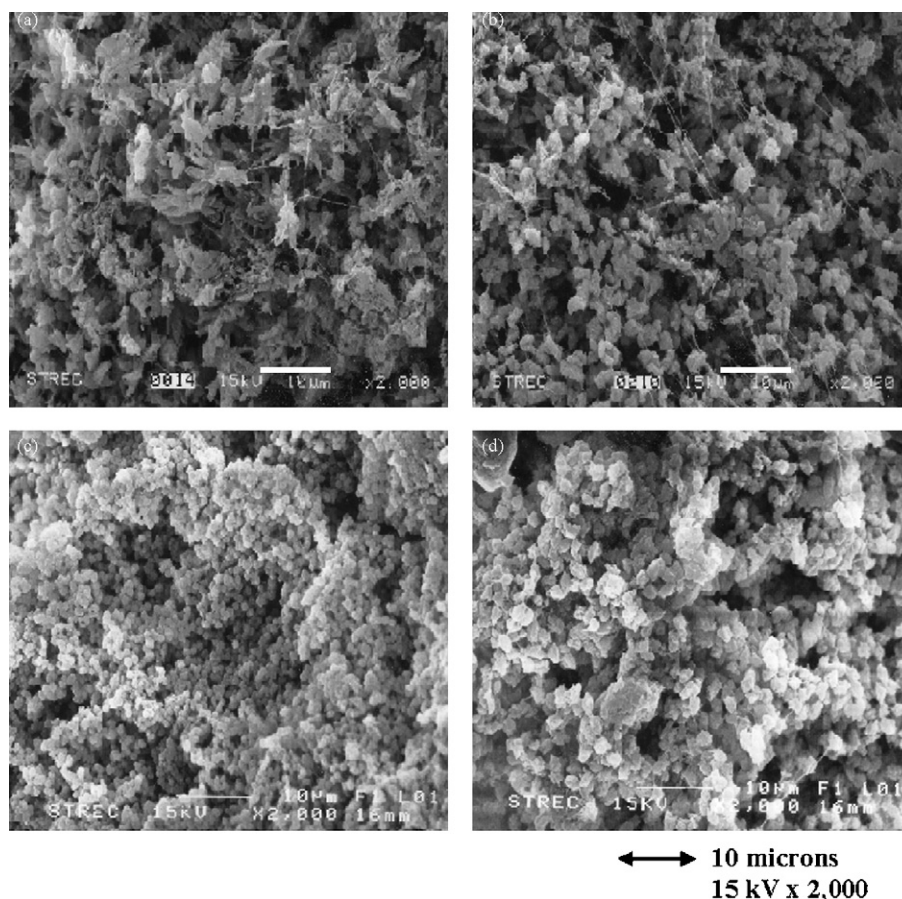


Fig. 7. SEM micrographs of polymers produced from: (a) homogeneous system, (b) TiO<sub>2</sub> support, (c) SiO<sub>2</sub> support, and (d) TiO<sub>2</sub>-SiO<sub>2</sub> support.

solvents favor ion-pair separation. The reason why the activity in these solvents is lower is most probably due to solvent coordination. On the other hand, the lower activity in heptane may reflect the lower solubility of the cationic catalyst and may not be reduced to ion-pair separation, and (ii) for the supported system, heptane gave the highest activity since the interaction between cationic and solvent was less than the interaction between cationic, anionic and monomer in the system. Plausible scheme for the interaction between active species and solvent are shown in Scheme 1 indicating (a) active species in heptanes, which is shown the effect of contact ion-pair having low dielectric constant and (b) active species in polar solvents, which is shown the effect of solvent-separated ion-pair. Therefore, the less polarity of solvent resulted in high polymerization activity.

#### 3.4. Effect of polymerization temperature on the catalytic activity

Fig. 6 shows the dependence of temperature on the catalytic activity. The effect of polymerization temperature via titanium complex with dMMAO was studied and the results obtained were compared with dMMAO/TiO<sub>2</sub>-supported system. Profiles in Fig. 6 reveal that both homogeneous and supported systems exhibit a volcano shape. It indicated that the homogeneous system displayed higher catalytic activity than that of supported system in all temperature. This system gave maximum catalytic activity at polymerization temperature at 323 K (5186 kg PE/(mol cat h)). In contrast dMMAO/TiO<sub>2</sub>-supported system exhibited the highest catalytic activity at 343 K (3727 kg PE/(mol cat h)). The catalytic activity decreased with increasing temperature probably due to the decomposition of the active species because of loss of the phenoxy-imine ligands from the titanium complex [13]. In fact, several mechanisms have been identified as decomposition pathways for cationic group 4 metal cations. Thus, based on this work it can be only concluded that the active species is thermally unstable.

#### 3.5. Properties of polymer

##### 3.5.1. SEM of polymers

Fig. 7 reveals that the polyethylene produced by the titanium complex with different supports, displays morphologies with well-defined particles, whereas that obtained from the homogeneous system exhibits ill-defined polymer morphologies. This observation indicates that the titanium complex immobilized on the surface of the different supports and hence, the polymerization takes place on the solid surface. It is known that the morphology of the polymer particles can be controlled by shapes of the support used [41].

##### 3.5.2. Thermal properties

Results of thermal behavior of polyethylene obtained from the differential scanning calorimetry (DSC) are shown in Table 1. These results suggested that for ethylene polymerization, the melting temperature ( $T_m$ ) ranged between 407 and 409 K. It indicated that there was no significant change in melting temperature ( $T_m$ ) upon different supports and solvents used.

## 4. Conclusion

In summary, we have demonstrated that the titanium complex having phenoxy-imine ligands (Ti–FI catalysts) can be activated using different supported-dMMAOs to give high-performance catalysts for the ethylene polymerization. It shows that the homogeneous catalyst displayed higher catalytic activity than that of the

supported system. The Ti–FI catalysts are capable of producing the highest polymerization activity when TiO<sub>2</sub>/dMMAO was employed. In addition, the Ti–FI catalysts can alter polymerization activity with different mediums employed. In order to give a better explanation, the contact ion-pair model under the typical polymerization condition was applied. There was no significant effect of different supports and solvents on the thermal properties of polymer obtained.

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